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## PROVISIONAL APPLICATION COVER SHEET

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This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(b)(2)

Docket Number		11495-1		Type a Plus Sign (+) inside this Box →		+	
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TITLE OF THE INVENTION (280 CHARACTERS MAX.)							
Exceptionally High Capacity Cathodes for Lithium Ion Batteries Based on Chemically Modified $\text{Li}_2\text{MnO}_3$							
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<input checked="" type="checkbox"/>	Specification	Number of pages	9	<input type="checkbox"/> Small Entity Statement			
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METHOD OF PAYMENT (Check One)							
<input type="checkbox"/>	A check or money order is enclosed to cover the Provisional filing fees					Provisional Filing Fee Amount (\$)	\$160.00
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The invention was made by an agency of the United States Government or under contract with an agency of the United States Government. ☒ No

Date:

27 May 2003

Respectfully submitted,

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Enclosures  
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Additional inventors are being named a separately numbered sheets attached hereto.

PROVISIONAL APPLICATION FILING ONLY

## Exceptionally High Capacity Cathodes for Lithium Ion Batteries Based on Chemically Modified $\text{Li}_2\text{MnO}_3$

### BACKGROUND OF THE INVENTION

5

Increasing demands are being placed on mobile powers sources to provide more power for longer periods between recharging. Lithium-ion batteries are the mainstay of this market, but the available power is limited. Manufacturers want to market increasingly complex and power-hungry appliances but the chemistry of the present cathode materials prohibit the increased energy density demanded. In addition to limited energy density, current materials have problems with regard to cost, environmental compatibility, and thermal safety.

10

Lithium ion batteries have become the prevalent power source for a broad range of portable electronic devices. In 2002, the lithium ion battery industry exceeded 2 billion dollars US in sales. Although they are rechargeable batteries, eventually even they must be disposed of. The suitability of these batteries for disposal in landfill is questionable. In addition, portable electronic devices containing lithium ion batteries are taken everywhere including on passenger aircraft. Consequently, safety is a major preoccupation of the manufacturers of these batteries and the devices that use them.

15

20

Most of the current productions of lithium ion batteries employ  $\text{LiCoO}_2$  as the active material in the cathode. A newer cathode material,  $\text{LiFePO}_4$ , is gradually being introduced into the market. Although it results in a lower energy density battery, it is gaining market acceptance for its enhanced safety characteristics.

25

Current materials do not provide the desired energy density. Some materials may be pushed to provide higher energy densities, but safety is a major concern for manufacturers, and frequently materials become thermally unstable under the conditions necessary to extract extra capacity.

30

There is growing competition from direct methanol fuel cells which offer greater energy density than the current lithium ion batteries. In addition, lithium ion batteries have been reported to have caused incidents of fires in laptop  
5 computers and other portable devices.

A number of papers and patents in related areas are available. With regard to the anomalous capacity of certain Ni-Mn systems the main references are:

- Lu & Dahn, J.Electrochem.Soc. v149 (2002), A815-822  
10 Shin *et al*, Journal of Power Sources, v112 (2002) 634-638

Materials in the complex Ni, Co, Mn systems, in particular the so-called 1/3:1/3:1/3 systems have been studied extensively by Ohzuku, who has both literature papers and a current patent application. He reports capacities of  
15 approximately 200 mAh/g with good thermal stability. Although some of the data bears a resemblance to that gathered from our materials, the capacities observed do not exceed the conventional theoretical capacity.

- Ohzuku *et al*, US Patent Application 10/242,052  
Yabuuchi and Ohzuku, Journal of Power Sources, in press  
20

Other papers have appeared which vary the ratios of Ni, Co and Mn, but do not venture into the Li-rich area.

- Wang *et al*, Journal of Power Sources, in press  
25 Lu *et al*, Electrochemical and Solid State Letters, v4 (2001), A200-203

The end-members of one series of materials have been described in two prior publications. These are 1:1 solid solutions of  $\text{Li}_2\text{MnO}_3$  and  $\text{LiNiO}_2$  or  $\text{LiCoO}_2$ , i.e.  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{O}_2$  and  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$ . One notable feature of these reports  
30 is that neither of them reported charging to high voltage, which is necessary to extract the anomalous capacities found in our study.

Numata *et al*, Solid State Ionics, v117 (1999), 257-263

Zhang *et al*, Journal of Power Sources, v110 (2002), 57-64

5 A US patent application, 09/799,935 of Paulsen et al., describes complex Li-rich systems. The examples cover a more limited range of compositions. In particular the maximum lithium content described in the examples is 1.16, and the cobalt contents are significantly lower than many produced in our work. The authors did not investigate the electrochemical performance of materials charged to voltages greater than 4.4 volts and consequently did not report any  
10 anomalous capacities.

Papers have described the behaviour of materials where Mn is replaced by Ti. Although at low levels  $\text{Li}_2\text{TiO}_3$  stabilises some materials, at high additions the discharge capacities drop as expected by the addition of an electrochemically  
15 'inert' material.

Zhang *et al*, Journal of Power Sources, v117 (2003), 137-142

The sucrose process used to produce many of these materials was reported by Das in 2001, and another paper co-authored by one of the applicants appeared  
20 in 2002.

Das, Materials Letters, v47 (2001), 344-350

Mitchell *et al*, Journal of Materials Science Letters, v21 (2002),  
1773-1775

## 25 SUMMARY OF THE INVENTION

Our proposal is to use a new type of cathode material based on modification of  $\text{Li}_2\text{MnO}_3$  that has an unusually large capacity for the reversible insertion of lithium ions at a useful voltage. Use of this type of material for the cathode will  
30 result in a battery with approximately 25% greater energy density. In addition,  $\text{Li}_2\text{MnO}_3$  is less expensive than to produce than  $\text{LiCoO}_2$  or  $\text{LiFePO}_4$ . Related

materials have been shown to have better safety characteristics than  $\text{LiCoO}_2$ , and there is a long history of alkaline batteries containing a chemically similar material,  $\text{MnO}_2$ , being disposed of in landfill without incidents.

- 5 Unusually high, or anomalous, capacities have been observed in the solid solutions of composition,  $\text{Li}_{1+\delta}\text{M}_{1-\delta}\text{O}_2$ , wherein M is a mixture of Mn and any combination of substitute metal cations, and  $\delta \geq 0$ , that have been charged to voltages between 4.4 and 5.0 volts versus the potential of metallic lithium. We have found that the anomalous capacities previously reported in the Mn-Ni
- 10 systems are a more general process than previously thought. There are a number of metal ions that can be substituted into such materials in place of, or in addition to, the Ni cations. These choices are based on "ionic radii", i.e. whether they can fit into the structure without unduly disrupting it. Cations that have been found as possible fits into similar structures include: all the first row
- 15 transition metals, Al, Mg, Mo, W, Ta, Si, Sn, Zr, Be, Ca, Ga, and P. The most probable candidates are the transition metals of the first row, such as Ti, V, Cr, Fe, Co, Ni and Cu, and other metals such as Al, Mg, Mo, W, Ta, Ga and Zr. Such compositions can exhibit unusually high capacity, in excess of the conventional theoretical capacities that are calculated on the basis of
- 20 conventional views on the accessible range of oxidation states. For example, it is conventionally assumed that neither  $\text{Mn}^{4+}$  nor  $\text{O}^{2-}$  will be oxidized under the conditions of the application. The capacities obtained from these materials is beyond that calculated using such assumptions. It is also possible to substitute other cations including electrochemically inert  $\text{Al}^{3+}$  and still obtain
- 25 high capacities and stable cycling. Even with the addition of 10%  $\text{Al}^{3+}$ , capacities equivalent to all the lithium being extracted from the structure on first charge were found, which should be impossible from conventional wisdom. The mechanism for the production of these anomalous capacities seems to lie with the  $\text{Li}_2\text{MnO}_3$ , or possibly the Mn, content, and the unusual stability of these
- 30 materials from undesirable reactions with the electrolyte at high voltages.

- Papers reporting the replacement of Mn with Ti do not report the unexpectedly high discharge capacities found with Mn. The addition of 'inert'  $\text{Li}_2\text{TiO}_3$  has a detrimental effect on the discharge capacities, whereas the supposedly 'inert'  $\text{Li}_2\text{MnO}_3$  does not as long as a 'forming' step at high voltage is carried out. In fact experiments have confirmed that  $\text{Li}_2\text{MnO}_3$  itself can be cycled electrochemically, only its poor electronic conductivity results in a slow 'formation' of substantial electrochemical activity only after a number of cycles.
- 10 A broad range of chemical modifications of  $\text{Li}_2\text{MnO}_3$  have been shown to have exceptionally large discharge capacities. Most of these compositions have never been reported previously and represent a series of novel materials.
- 15 Some of the compositions tested produce capacities that can not be explained conventionally. Preliminary results also indicate an unusual ability to tune the discharge voltage through relatively small variations in the composition.
- 20 Some of the more complex materials made have 5 different species sharing a single crystallographic site. Many standard synthetic techniques would not provide sufficient homogeneity to achieve a single-phase material. The synthetic techniques used to date to achieve this level of homogeneity are a sucrose-based dispersion/combustion technique and high-energy ball-milling. The sucrose method has been modified slightly from that originally reported in the literature, and is easily capable of producing complex oxide materials with
- 25 crystallites of sizes  $< 100\text{nm}$ .

#### BRIEF DESCRIPTION OF THE DRAWINGS

- 30 Figure 1 illustrates X-ray diffraction patterns of materials calcined at  $800^\circ\text{C}$ ;

Figure 2 illustrates a variation of crystallographic strain in the different materials temperature and ratio of  $M'$  to  $M''$ ;

Figure 3 illustrates discharge capacities of materials calcined at  $740^{\circ}\text{C}$  with different  $M':M''$  ratios (2.0-4.6V, 10mA/g);

5 Figure 4 illustrates discharge capacities of materials calcined at  $800^{\circ}\text{C}$  with different  $M':M''$  ratios (2.0-4.6V, 10mA/g);

Figure 5 illustrates room temperature and  $55^{\circ}\text{C}$  electrochemical data for  $M'/(M'+M'') = 0.00$  calcined at  $800^{\circ}\text{C}$ . First cycle at  $55^{\circ}\text{C}$ , 4.6-2.0V, subsequent cycles 4.4-2.5V;

10 Figure 6 illustrates Discharge capacities at  $55^{\circ}\text{C}$  for  $M'/(M'+M'') = 0.25$  material calcined at  $800^{\circ}\text{C}$ . First cycle 4.6-2.0V, subsequent cycles 4.4-2.5V (10mA/g); and

Figures 7 to 17 illustrate the electrochemical performance and characteristics of various complex materials according to the invention.

15

#### DETAILED DESCRIPTION OF THE INVENTION

The stabilization of layered Mn-based cathode materials by the introduction of the electrochemically inert  $\text{Mn}^{4+}$  ion, has been one of the more recent  
20 innovations in efforts to develop more environmentally and economically acceptable materials for use in lithium-ion batteries.

The inclusion of  $\text{Mn}^{4+}$  has been reported to increase thermal stability, voltage stability, high temperature cyclability and discharge capacities. Given  
25 the increasing importance of safety in commercial battery materials, such materials are a fruitful area for further investigation.

The 1:1 solid solution of  $\text{LiCrO}_2\text{:Li}_2\text{MnO}_3$ ,  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$  exhibited very good electrochemical <sup>1</sup> and thermal characteristics,<sup>2</sup> with a reversible Cr(III)-  
30 Cr(VI) redox couple providing the capacity.<sup>3</sup> In addition to the unusual redox behaviour this material performs well, despite both of its end-members being poor electrical conductors. Another recent development in the search for high



capacity cathode materials are materials related to  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ,<sup>4</sup> which have been reported to yield stable discharge capacities of greater than 200 mA/g when cycled between 2.5-4.6V, and have good safety characteristics.

5

The results presented here pertain to a systematic study of  $\text{Li}_{1+\delta}(\text{Mn}, \text{M}', \text{M}'')_{1-\delta}\text{O}_2$  where  $\delta \geq 0$ , and  $\text{M}'$  and  $\text{M}''$  are transition metal or other metal cations. In each case the lithium and/or metal contents were engineered to produce a  $\text{Mn}^{4+}$ -containing material. These materials are  
10 complex, with up to 4 cations sharing a single site. Consequently a synthetic technique was chosen that allowed for an intimate and uniform mixing of the cations. The materials were produced by a combined dispersion/combustion synthetic technique that was developed for the production of nano-particulate oxides.<sup>5,6</sup> The method has previously been successful in the production of  
15 highly crystalline nanoparticulate  $\text{LiMn}_2\text{O}_4$  on a hotplate.<sup>7</sup>

Metal nitrates in the stoichiometric proportions required were dissolved in water with a 4:1 molar excess of sucrose. The solution was then acidified with concentrated nitric acid to a pH below 1. Heating then commenced,  
20 firstly to evaporate water, then to decompose the nitrates, and finally to foam, char, and oxidize the carbonaceous sucrose matrix. The resultant ash precursors were subsequently calcined in air, since the precursors contained residual  $\text{Li}_2\text{CO}_3$  that must be reacted further. Contamination of the materials is minimal, as there are no salts to wash out. The lithium is not added in a  
25 separate step, so sample inhomogeneity is not a problem.

The as-synthesised materials were studied by a variety of techniques, including Rietveld structure and microstructure analysis of powder X-ray diffraction data, galvanostatic cycling at room temperature and at 55°C, high  
30 resolution FEG-SEM, BET and AA.

Materials calcined at 740, 800 (see figure 1) and 900°C all appeared to be single phase. The materials showed trends in most structural parameters with changing M':M'' ratio. The crystallographic strain was anomalous in this respect as shown in figure 2. There does seem to be a correlation between the strain and some of the cycling behaviour of the materials.

The materials show a variety of microstructures when examined by FEG-SEM with varying degrees of sintering/agglomeration and large variations in particle sizes. The observed particle sizes agree well with crystallite sizes calculated from X-ray data and are therefore assumed to be the primary particles in the material.

The discharge capacities of the materials calcined at 740 and 800°C are shown in figures 3 and 4. Many of the materials exhibit capacities around and above 200 mAh/g with satisfactory capacity retention found for many of the compositions. The  $M'/(M'+M'') = 0.0$  material is noticeable from the differences in behaviour between material calcined at 740 and 800°C. It is hypothesised that this difference is kinetic in nature, and this is supported by electrochemical data obtained at 55°C (figure 5). Many compositions have been found to cycle in a very stable manner at 55°C, as is shown in figure 6.

In conclusion, a series of materials have been produced that exhibit capacities of up to 200 mAh/g at room temperature. Some of these compositions show good capacity retention over the number of cycles studied to date. Work has been presented on the development of the materials in terms of synthesis routes, phase behaviour and electrochemical characteristics. Data will be presented for a number of voltage windows and current conditions to demonstrate the materials' possible use in a commercial application.

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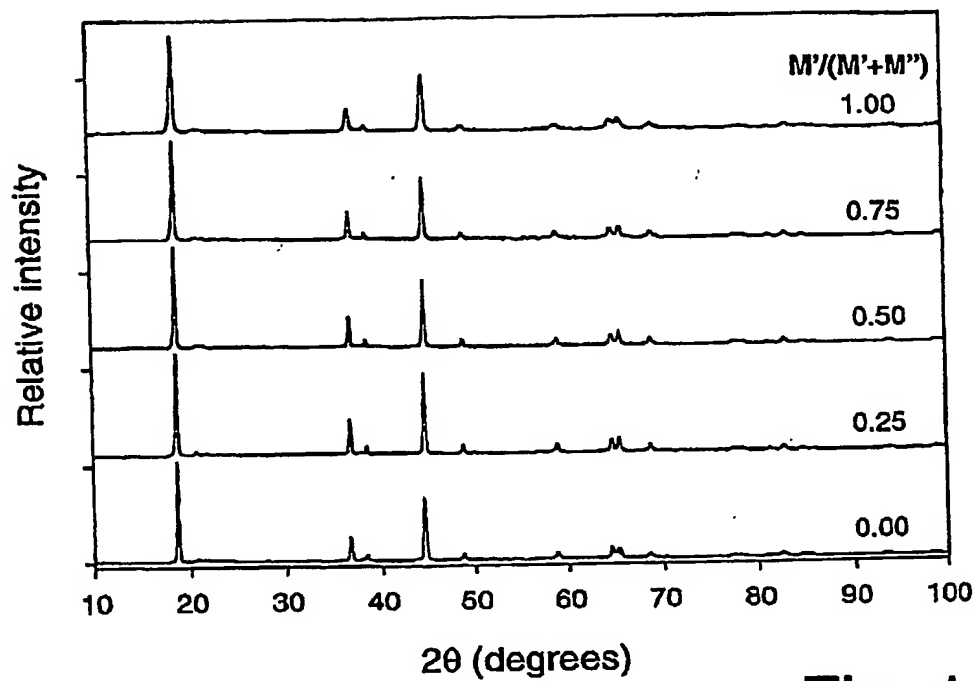


Fig. 1

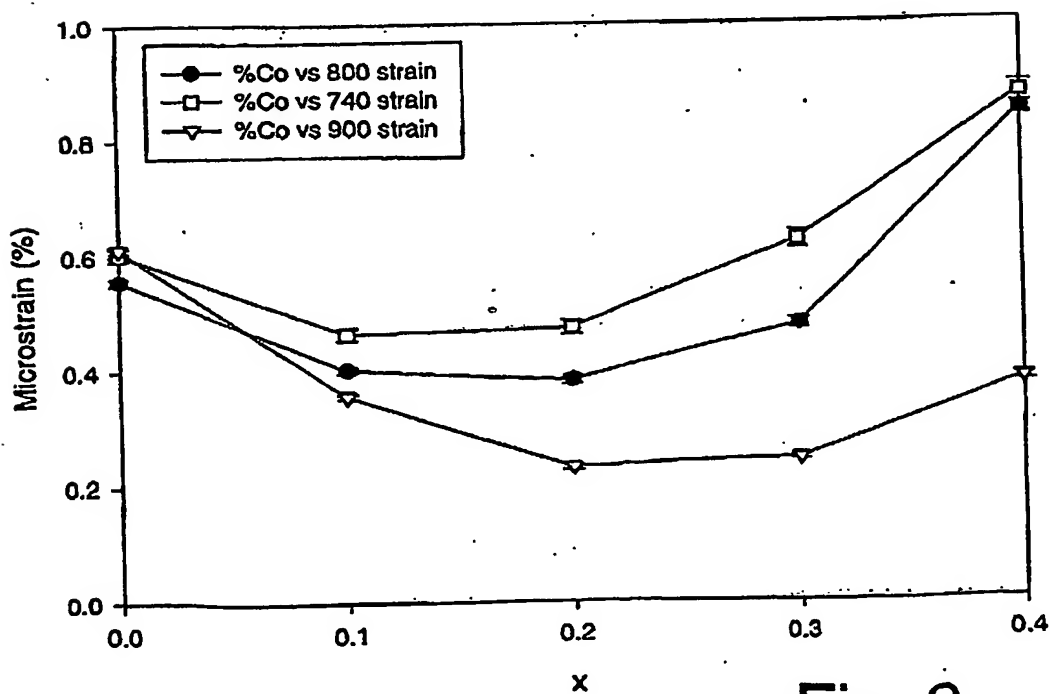


Fig. 2

$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.4-x}\text{Co}_x\text{O}_2$  (800°C)  
2.0-4.6V, 10mA/g

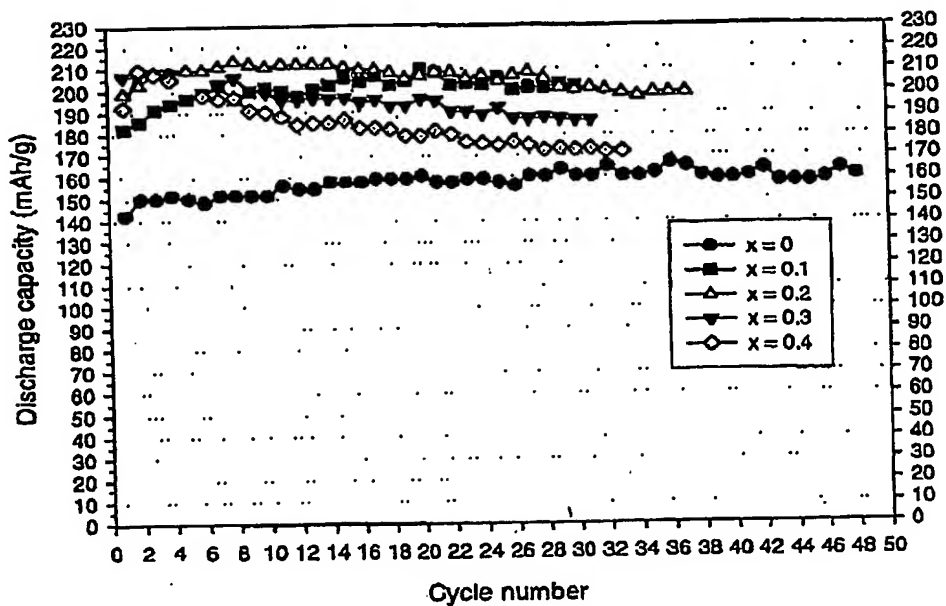


Fig. 3

$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.4-x}\text{Co}_x\text{O}_2$  (740°C)  
2.0-4.6V, 10mA/g

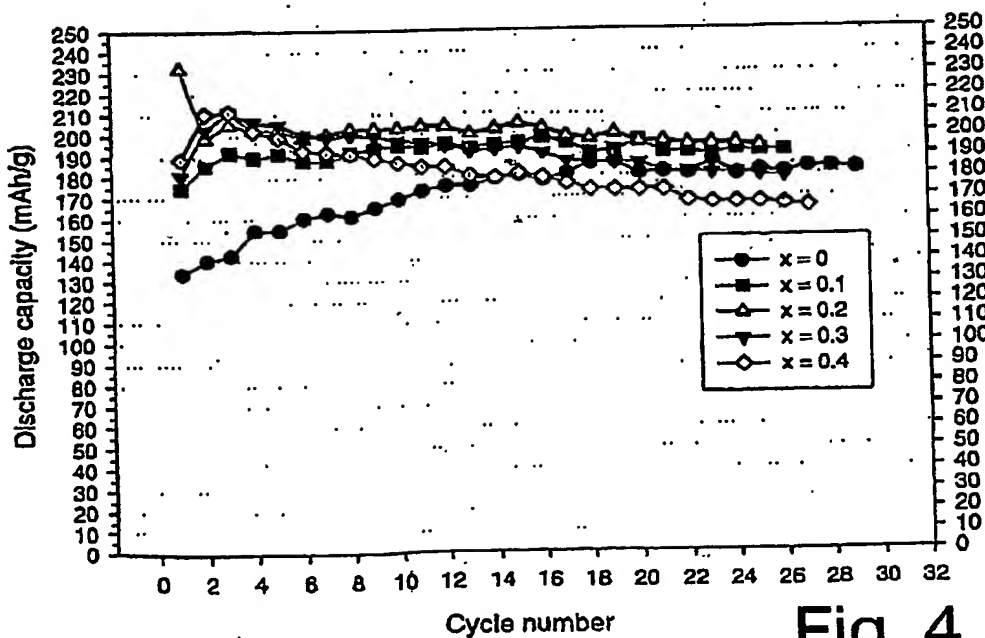


Fig. 4

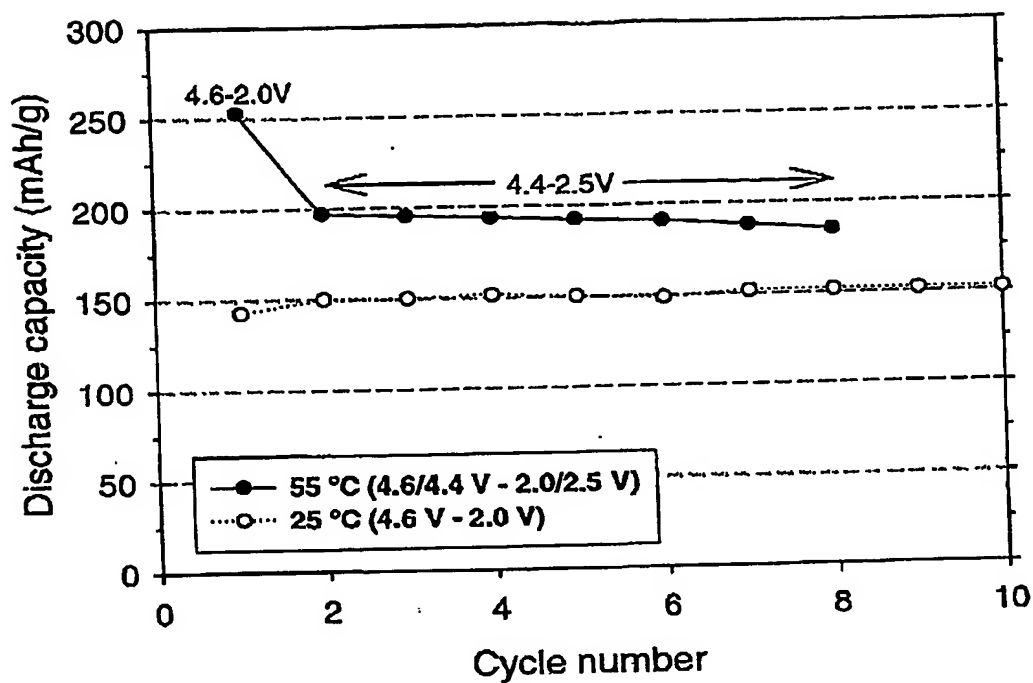


Fig. 5

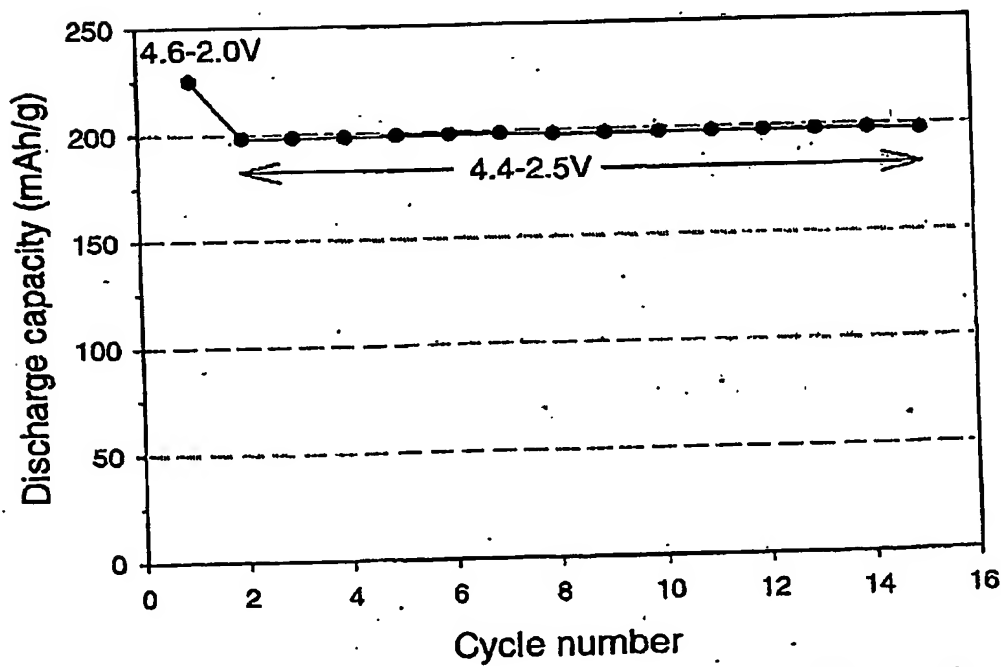
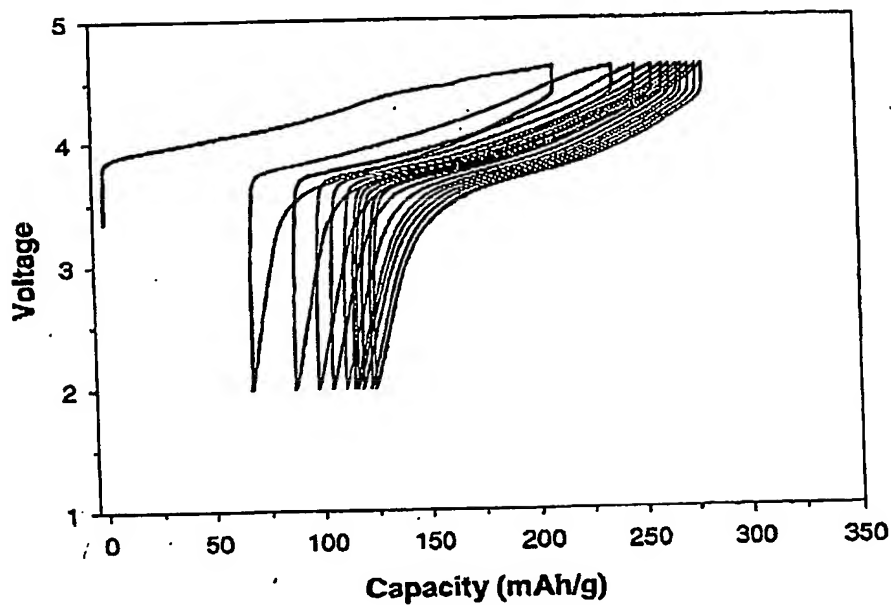


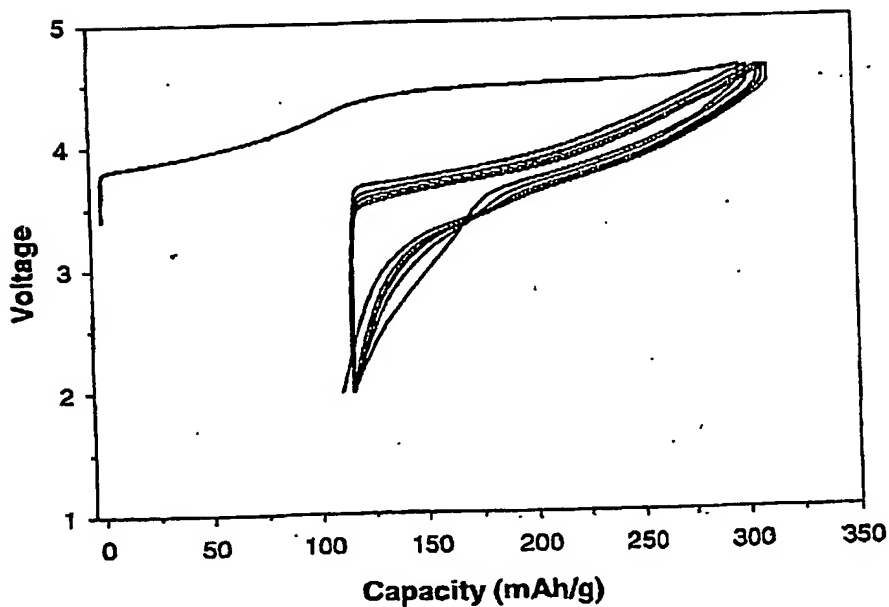
Fig. 6

**PCNM40 (PW08p36a - 800°C)**  
 **$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{O}_2$**   
**2.0-4.6V**



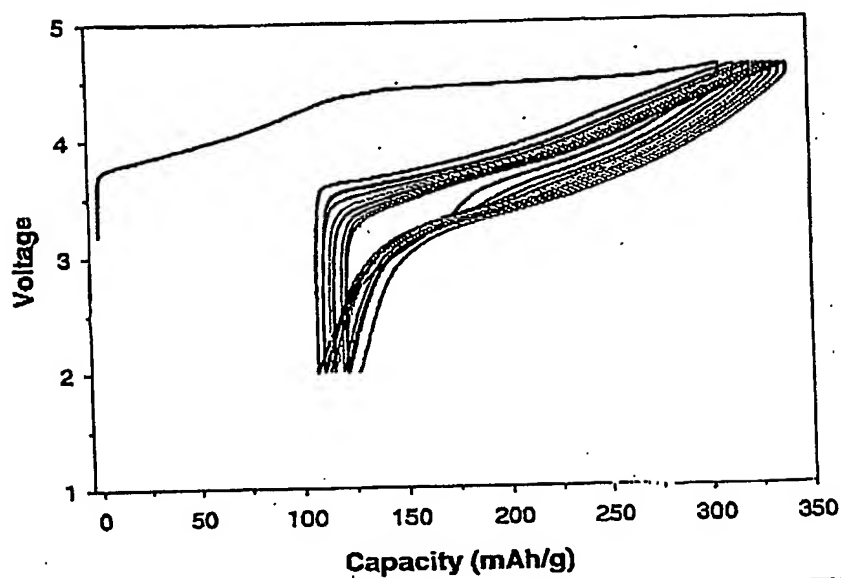
**Fig. 7**

**PCNM42 (PW08p41a - 800°C)**  
 **$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.3}\text{Co}_{0.1}\text{O}_2$**   
**2.0-4.6V, 10mA/g**



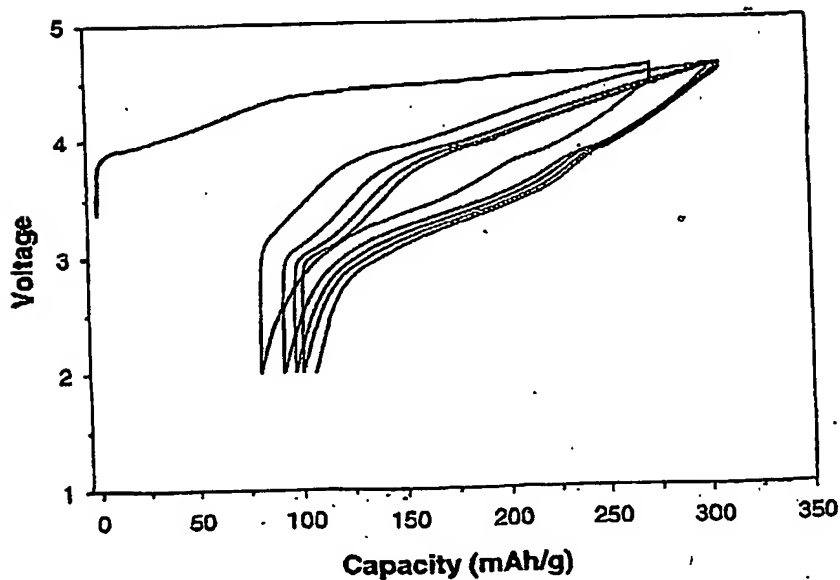
**Fig. 8**

**PCNM38 (PW08p34a - 800°C)**  
 **$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.2}\text{Co}_{0.2}\text{O}_2$**   
**2.0-4.6V**



**Fig. 9**

**PCNM46 (PW08p47a - 800°C)**  
 **$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$**   
**2.0-4.6V, 10mA/g**



**Fig. 10**



Cycle 1

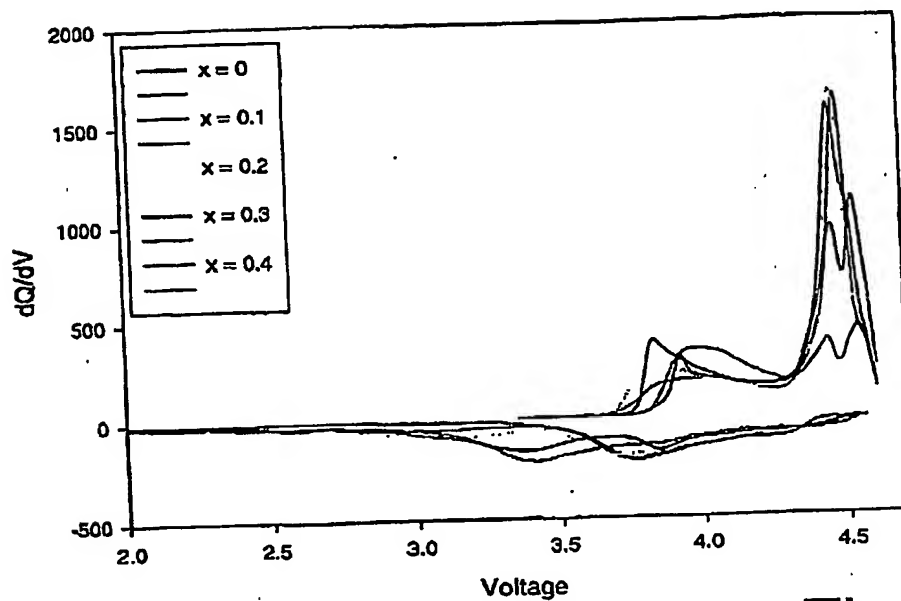


Fig. 11

Cycle 5

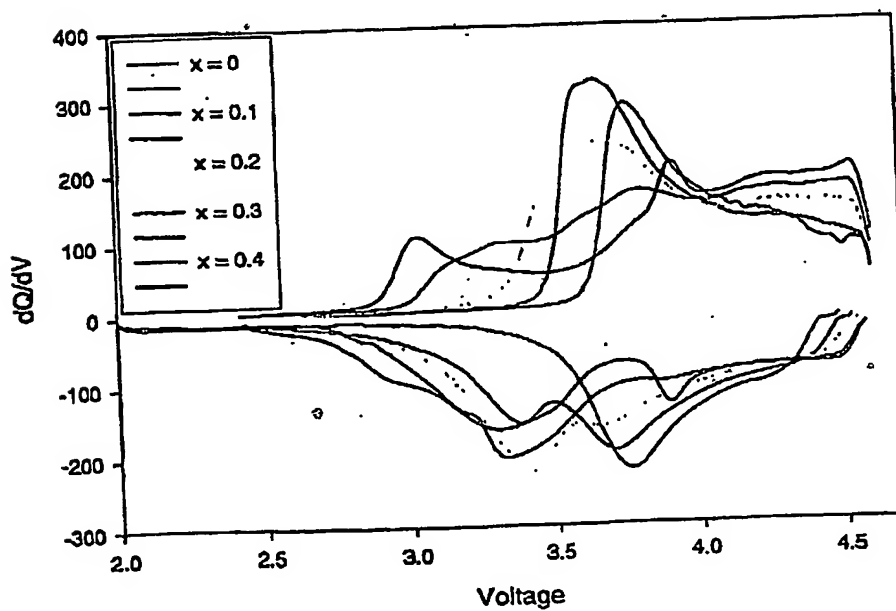


Fig. 12

Cycle 10

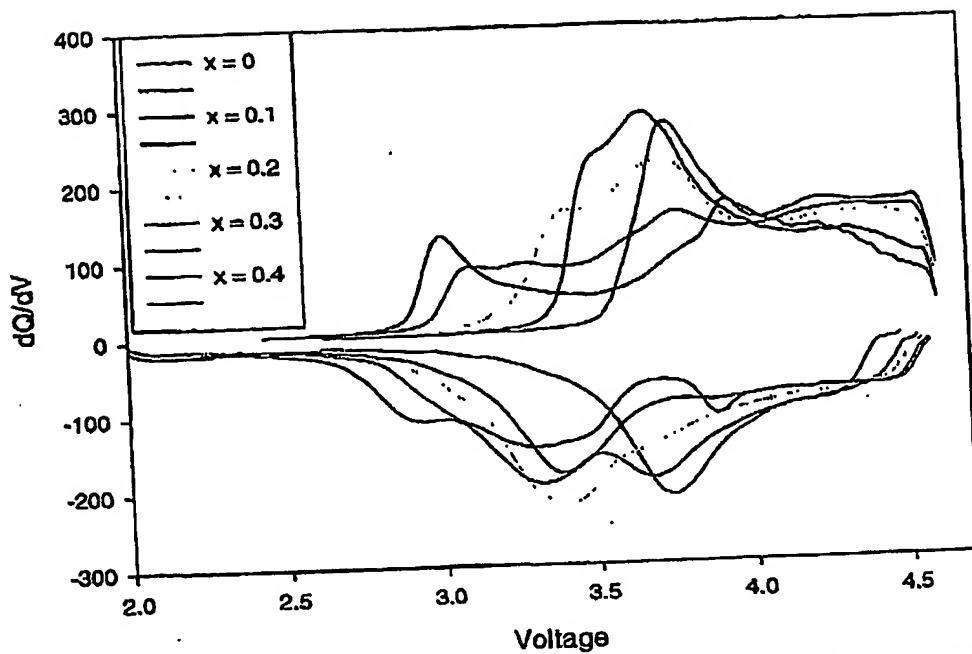


Fig. 13

Cycle 15

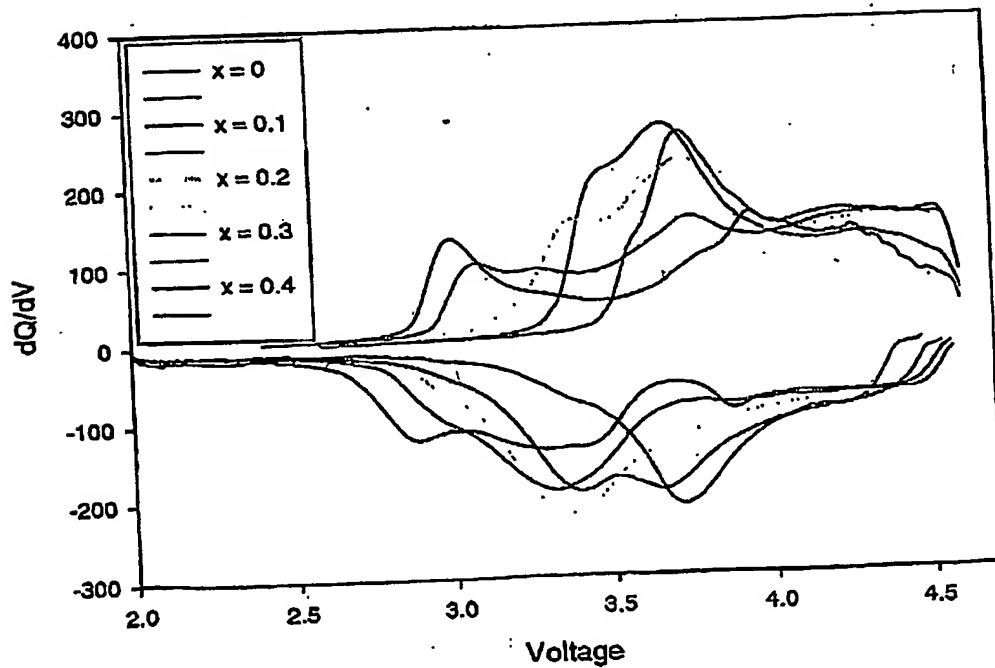


Fig. 14

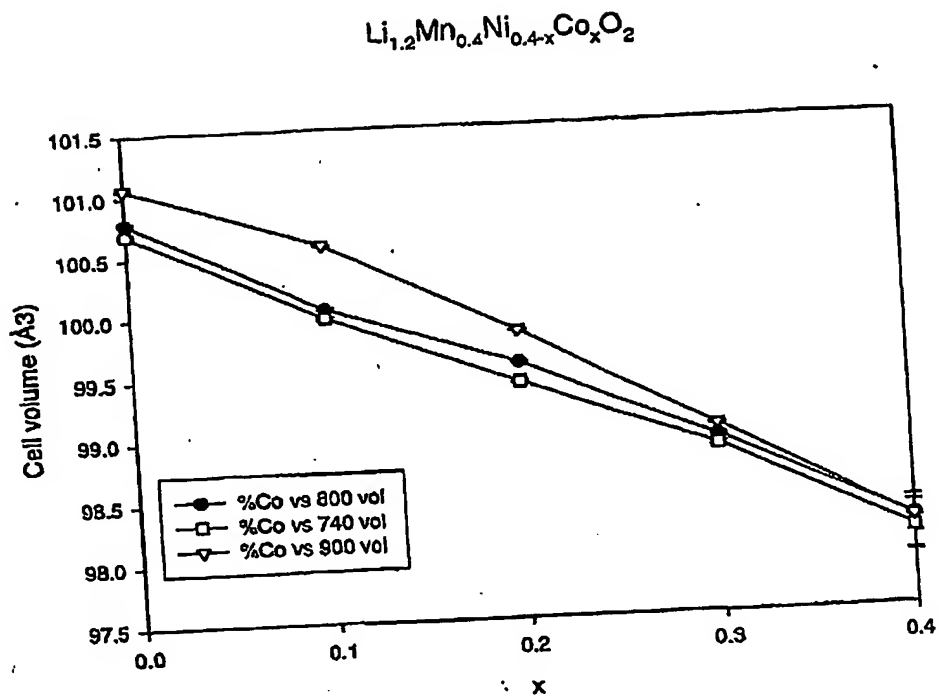


Fig. 15

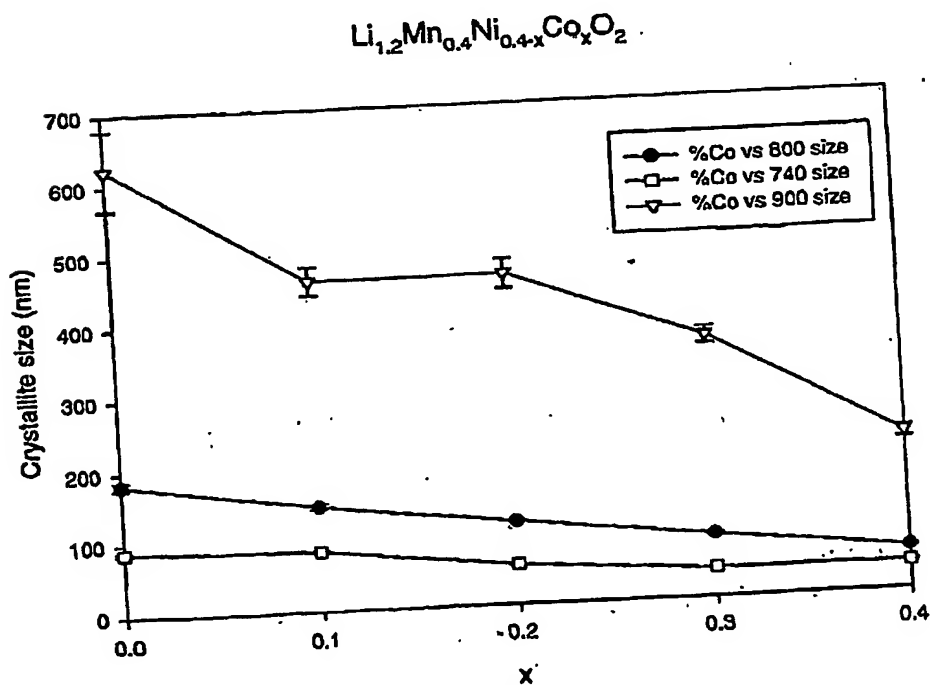


Fig. 16

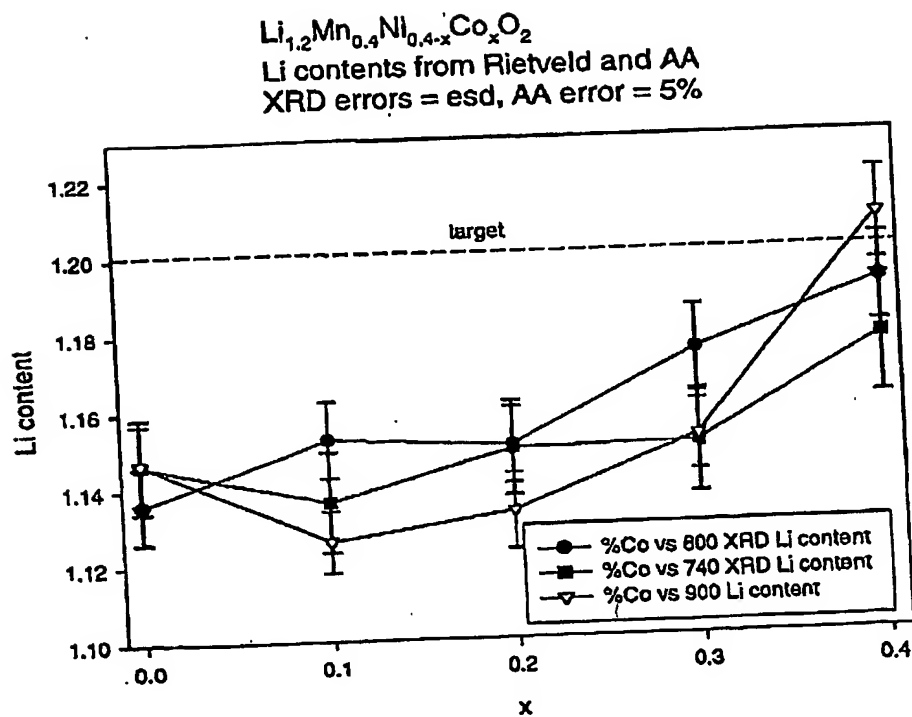


Fig. 17